THE SYNTHESIS OF HIGHER CYCLOMETHYLALKYLSILAZANES

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The ammonolysis of dichloro(isobutyl)methylsilane and dichloro(methyl)(nonyl)silane forms triisobutyltrimethylcyclotrisilazane, tetraisobutyltetramethylcyclotetrasilazane, and trimethyltrinonylcyclotrisilazane. The coammonolysis of dichloro(isobutyl)(methyl)silane with trichloro(nonyl)silane gave a cyclic compound with free amino groups—3,7-diamino-1,1,5,5-tetraisobutyl-1,1,5,5-tetramethyl-3, 7-dinonylcyclotetrasilazane—and the coammonolysis of dichloro(isobutyl)(methyl)silane with trichloro-(isobutyl)silane yielded bicyclic products—1,3,5,7-tetraisobutyl-1,5-dimethylbicyclotetrasilazane and 1,3,5,7,9-pentaisobutyl-1,5,7-trimethylbicyclopentasilazane.

The ammonolysis and coammonolysis of the higher dialkyldichloro- and alkyltrichlorosilazanes have been studied inadequately. There is some information only on the ammonolysis of some higher alkyltrichlorosilanes [1]. It appeared of interest to study these reactions with higher dialkyldichloro- and alkyltrichlorosilanes and to trace the influence of the size of the radical on ammonolysis and coammonolysis reactions. As the initial chlorosilanes we used dichloro(isobutyl)(methyl)silane and dichloro(methyl)nonylsilane. The ammonolysis of dichloro(isobutyl)methylsilane takes place in accordance with the scheme:

$$ni\text{-}C_4H_9(CH_3)SiCl_2 + 3nNH_3 \rightarrow$$

$$\rightarrow m\underset{\text{I}}{[i\text{-}C_4H_9(CH_3)SiNH]_3} + {}^1\!/_4(n-3m)\underset{\text{II}}{[i\text{-}C_4H_9(CH_3)SiNH]_4} + 2nNH_4Cl$$

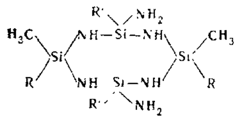
The ammonolysis of dichloro(isobutyl)methylsilane yielded triisobutyltrimethylcyclotrisilazane (I) with a yield of 45% and tetraisobutyltetramethylcyclotetrasilazane (II) with a yield of 15%. The ammonolysis of dichloro(methyl)(nonyl)silane took place similarly, but in this case it was possible to isolate only about 44.5% of trimethyltrinonylcyclotrisilazane $[C_9H_{19}(CH_3)SiNH]_3$ (III).

The properties of the heterocycles synthesized are given in the table. To confirm their structure, their IR spectra were recorded, and these showed absorption bands in the following regions: 927–931 cm^{-1} ($\nu_{Si-N-Si}$), 1166–1182 cm^{-1} (δ_{N-H}), and 3400 cm^{-1} (ν_{asNH}) [2].

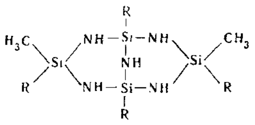
The coammonolysis of dichloro(isobutyl)(methyl)silane with trichloro(nonyl)silane in a molar ratio of 1 : 1 formed both products of separate ammonolysis (19.5% of I and 12.4% of II) and a product of coammonolysis—3,7-diamino-1,5-diisobutyl-1,5-dimethyl-3,-7-dinonylcyclotetrasilazane (IV) (yield 29.8%)—together with undistillable coammonolysis products (28.4%). The IR spectrum of IV showed—in addition to the $\nu_{Si-N-Si}$ bands in the 927–931 cm^{-1} region, δ_{N-H} in the 1166–1182 cm^{-1} region, and ν_{asNH} in the 3400 cm^{-1} region—another absorption band in the 3485 cm^{-1} region which is characteristic for the NH_2 group.

The coammonolysis of dichloro(isobutyl)(methyl)silane with trichloro(isobutyl)silane again yielded both products of separate ammonolysis—21.5% of I and 15.4% of II—and products of coammonolysis—8.5% of 1,3,5,7-tetraisobutyl-1,5-dimethylbicyclotetrasilazane (V) and 10.5% of 1,3,5,7,9-pentaisobutyl-1,5,7-trimethylbicyclopentasilazane (VI), together with undistillable products (32%).

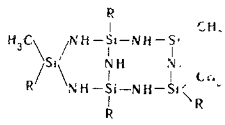
The compounds obtained in this case were distinguished from IV by the fact that they contained no free amino groups. The analytical results and the IR spectra, in which there are absorption bands of $\nu_{Si-N-Si}$ in the 927–931 cm^{-1} region, δ_{N-H} in the 1166–1182 cm^{-1} region and ν_{asNH} in the 3400 cm^{-1} region, show that the products of the coammonolysis of dichloro(isobutyl)(methyl)silane with trichloro(isobutyl)silane are the bicyclic compounds:



IV



V



VI

R = i-C_4H_9, R' = C_9H_{19}

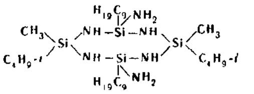
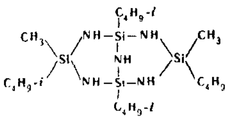
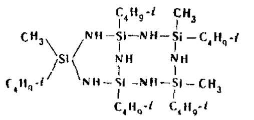
Apparently, the size of the organic radical on the silicon atom has an effect on the structure of the cyclic compounds formed. In the product of the coammonolysis of dichloro(isobutyl)(methyl)silane with trichloro(nonyl)silane the further participation of the amino groups in the reaction is made difficult by steric hindrance.

EXPERIMENTAL

Ammonolysis of dichloro(isobutyl)(methyl)silane. The ammonolysis was carried out in a four-necked flask fitted with a stirrer, reflux condenser, thermometer, and tube for the introduction of ammonia; this was charged with a solution of 144.7 g of dichloro(isobutyl)(methyl)silane (bp 138–142° C, 41.4% Cl) in 600 ml of absolute benzene, and dry ammonia was bubbled through it until the reaction with the dichloro(isobutyl)(methyl)silane was complete. The temperature of the reaction mixture was kept at about 20–25° C. After the ammonium chloride had been removed, treatment with 2% KOH solution and elimination of the solvent by distillation yielded 63 g of a clear fairly viscous liquid (22.7 g), the vacuum distillation of which gave 12 g of triisobutyltrimethylcyclotrisilazane (I) and 4.5 g of tetraisobutyltetramethylcyclotetrasilazane (II).

Ammonolysis of dichloro(methyl)(nonyl)silane. The ammonolysis of a solution of 50 g of dichloro(methyl)(nonyl)silane [bp 95–105° C (1 mm); 29.4% Cl] in 300 ml of anhydrous petroleum ether was carried out by the method described above. After the elimination of the ammonium

Physicochemical Properties of the Alkylmethylcyclosilazanes

Compound	Formula	Bp, °C (1 mm)	n_D^{20}	d_4^{20}	M		Empirical formula	Found, %				Calculated, %				Yield, %
					found	calculated		C	H	N	Si	C	H	N	Si	
I	$[CH_3(i\text{-}C_4H_9)SiNH]_3$	131—132	1.4570	0.9050	345	342	$C_{15}H_{39}Si_3N_3$	51.35	10.99	12.2	24.08	52.6	11.4	12.4	24.4	45
II	$[CH_3(i\text{-}C_4H_9)SiNH]_4$	141—142	1.4580	0.9012	455	461	$C_{20}H_{52}Si_4N_4$	52.45	11.42	12.07	23.59	52.10	11.37	12.4	24.6	15
III	$[CH_3(C_9H_{19})SiNH]_3$	233—234	1.4685	0.8879	557	556	$C_{30}H_{69}Si_3N_3$	65.73	13.13	7.59	14.79	65.3	12.5	7.55	15.1	44.5
IV		167—168	1.4685	0.9338	612	600	$C_{28}H_{70}Si_4N_6$	54.26	11.54	13.61	20.74	55.9	11.6	13.9	18.6	28.9
V		164—165	1.4705	0.9546	440	445	$C_{18}H_{47}Si_4N_5$	49.88	11.12	15.2	24.15	48.47	10.62	15.7	25.14	8.5
VI		224—226	1.4758	0.9575	575	561	$C_{23}H_{70}Si_5N_6$	48.52	11.02	15.02	25.13	49.22	10.77	14.98	25.03	10.6

chloride and the distillation of the solvent, 32 g of a clear liquid was obtained. The vacuum distillation of 11.5 g of it yielded 5.1 g (44.5%) of trimethyltrinonylcyclotrisilazane (III).

Coammonolysis of dichloro(isobutyl)(methyl)silane with trichloro(nonyl)silane. The reaction was carried out by a similar method. At a molar ratio of dichloro(isobutyl)(methyl)silane to trichloro(nonyl)silane of 1 : 1, a solution of 68.3 g of dichloro(isobutyl)(methyl)silane and 110.15 g of trichloro(nonyl)silane in 500 ml of petroleum ether was used. After the ammonium chloride and the solvent had been eliminated, 80 g of a clear liquid was obtained. The distillation of 11.8 g of this in vacuum gave 3.6 g (19.5%) of triisobutyltrimethylcyclotrisilazane, 2.3 g (12.4%) of tetraisobutyltetramethylcyclotetrasilazane (II), and 5.5 g (29.8%) of coammonolysis product—3,7-diamino-1,1,5,5-tetraisobutyl-1,1,5,5-tetramethyl-3, 7-dinonylcyclotetrasilazane (III).

Coammonolysis of dichloro(isobutyl)(methyl)silane with trichloro(isobutyl)silane. Ammonia was passed into a solution of 58 g of dichloro(isobutyl)(methyl)silane and 64 g of trichloro(isobutyl)silane (bp 139–142° C; 50.6% Cl) in 600 ml of petroleum ether. After the elimination of the precipitate of NH_4 Cl (by treating the reaction mixture with 2% KOH solution), and the distillation of the solvent, 65.62 g (84%) of a clear fairly viscous liquid was obtained. When 17 g of this was distilled in vacuum, 6.5 g of products of separate ammonolysis (I and II) and two bicyclic products of coammonolysis (V and VI) was obtained.

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